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<b>(21) International Application Number:</b> PCT/US99/00870 <b>(22) International Filing Date:</b> 15 January 1999 (15.01.99)  <b>(30) Priority Data:</b> 09/018,583      4 February 1998 (04.02.98)      US  <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  <b>(72) Inventors:</b> ALI, Mahfuza, B.; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LEIR, Charles, M.; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LOTTES, Andrew, C.; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). SARKAR, Manisha; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). WILLIAMS, Donald, J.; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  <b>(74) Agents:</b> FONSECA, Darla, P. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> CA, JP, MX, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> INK RECEPTIVE SHEET  <b>(57) Abstract</b>  An imageable sheet having a substrate coated on at least one side with a universal imaging coating formed from a latex emulsion containing up to 10 mol % of a monomer possessing cationic or quaternary ammonium functionality, and which in addition may contain greater than 10 mol % of a monomer having hydroxy functionality.		

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## INK RECEPTIVE SHEET

### Field of the Invention

The invention relates to materials that are useful as ink-receptive sheets for imaging, especially transparent materials having ink-receptive layers which exhibit improved curl and mordant properties.

### Description of the Related Art

Imaging devices such as ink jet printers and pen plotters are established methods for printing various information including labels and multi-color graphics. Presentation of such information has created a demand for ink-receptive imageable sheets useful for commercial graphics, and for transparent ink receptive imageable receptors that are useful as overlays in technical drawings and as transparencies for overhead projection.

Imaging with either the ink jet printer or the pen plotter involves depositing ink on the surface of these receptors. These imaging devices conventionally utilize inks that can remain exposed to air for long periods of time without drying out.

Since it is desirable that the surface of these receptors be dry and non-tacky to the touch soon after imaging, even after the absorption of significant amounts of liquid, desirable imaging receptors are transparent materials that are capable of absorbing significant amounts of liquid while maintaining some degree of durability and transparency.

Compositions useful as liquid-absorbent receptors have been formed by blending and coating a liquid-soluble polymeric material with a liquid-insoluble polymeric material. For example, U.S. Patent No. 4,371,582 discloses an ink jet recording sheet having an ink receptive layer containing a basic latex polymer and other water soluble polymers such as gelatin wherein the latex preferably includes at least 10 mol% of a copolymerizable monomer having a tertamino or a quaternary ammonium group.

U.S. Patent No. 4,578,285 discloses an ink jet printing sheet with a transparent support bearing a layer containing a major proportion of a polyurethane latex and a minor proportion of a water soluble polymer.

U.S. Patent No. 4,849,286 discloses a plotter film having an ink receptive coating comprising from 40 to 65 percent by weight of a polyurethane latex.

Many basic polymers may be included in ink receptive layers for ink jet recording, as well as basic nonpolymeric materials. For example, U.S. Patent No. 5,589,269 discloses a polymeric mordant containing, as an active entity, a guanidine function. U.S. Patent No. 5,518,821 discloses an ink jet recording medium comprising a water-soluble quaternary ammonium polymer and compounds and polymers containing multiple hydroxy groups.

U.S. Patent No. 4,554,181 discloses an ink jet recording sheet containing a combination of a water soluble polyvalent metal salt and a cationic polymer, the cationic groups being present for the insolubilization of an anionic dye such as is likely to be present in an ink jet ink. In this case "insolubilization" may be considered to be equivalent to the term "mordanting". It is generally believed that the anionic dyes present in ink jet inks form a salt with the quaternary ammonium entity that is either water insoluble or of such a large size that diffusion in the polymeric matrix is reduced or eliminated.

U.S. Patent No. 4,740,420 claims a recording medium for ink-jet printing that contains a cationic organic material selected from the classes of alkyl amines, quaternary ammonium salts and polyamines.

European Patent Application 0 767 071-A discloses an ink jet recording sheet containing a pigment and a binder, the binder being a self-emulsifying cationic resin consisting of essentially of at least one water-insoluble acrylic copolymer having cationic functional groups.

European Patent Application 0 763 433 A2 claims an ink jet recording medium containing at least one nitrogen-containing component. The nitrogen-containing component is to be selected from poly(vinylpyrrolidone), polyimines, gelatins or quaternary polymers. It should be assumed that one or more of these nitrogen-containing entities can function at least partially as a mordant.

Ink jet recording media are also known to contain materials best described as plasticizers. These plasticizers are materials whose primary function is to control mechanical properties of the final film. By mechanical properties, it is meant those characteristics that do not influence image characteristics such as color, brightness, bleed, and resolution. A mechanical property of importance to the user of ink jet films is curl. Curl is regarded as undesirable in that films having this characteristic may not lay flat on

the stage of an overhead projector, or may not be easy to store, or to feed into imaging devices such as printers. In extreme cases, films with humidity-dependent curl have been known to burst packaging. Small amounts of curl may be acceptable, if still generally undesirable.

5 U.S. Patent No. 5,118,570 discloses coatings for ink jet receptors that contain plasticizers selected from the group of propylene glycol, propylene glycol monostearate, diethylene glycol and ethylene carbonate. U.S. Patent No. 5,006,407 selects plasticizers that in addition to those of U.S. Patent No. 5,118,570, include phosphates, substituted phthalic anhydrides, pyrrolidinones and others.

10 Japanese Kokai No. Sho 62[1987]-156984 discloses an ink-jet recording method using a recording material characterized by containing a compound that has both 3 or more hydroxy groups and a molecular weight of 500 or less on the recording surface. This material was disclosed to provide good ink absorbency dot shape and high resolution. The material may be coated onto paper or synthetic film substrates.

15 As might be expected, other imaging devices such as laser printers and xerographic copying machines, and color copiers have differing requirements, such as heat resistance, toner adhesion, and image haze. Thus, materials which are designed for use with one type of imaging device are frequently, if not useless with other imaging devices, less useful, having been optimized for one type of device. If imageable, the  
20 image may be of lesser quality, lesser resolution, lack shelf stability, etc.

Electrophotographic copying machines require materials for which the coefficient of friction must be controlled within a certain range. Very low Coefficients of Friction cause difficulty in handling, the sheets being too slippery. High Coefficients of Friction may prevent the top sheet of a stack being removed in the process of feeding. Thus the  
25 surface of the sheets are adjusted to be in an intermediate range. Such adjustment is most easily performed by the addition to the surface coating of a suitable particulate. A lubricant may also be included.

Nor is this problem of compatibility solved by simply adding additional components to the coating material. The addition of many components to a coating  
30 formulation, with each one controlling a particular characteristic of the final product may result in dilution of the effective value of one or more particular components. Addition of a sufficient quantity of a component to achieve a desired result may, practically, result

in the inability of the formulation to accommodate the desired amount of a second additive. It is therefore desirable to seek additives that are effective in small amounts in a formulation, and/or which combine the valuable effects of two or more additives. Thus with a small amount of a selected additive, the formulation may be brought to an overall higher level of performance than might be achieved were two separate additives, required in larger amounts, to be used.

It has now been discovered that use of a cationic latex emulsion having less than 10 mol% of a copolymerizable monomer having a tertamino or a quaternary ammonium functionality, and an average particle size of from 50 nm to 400 nm provides an imageable coating with good imaging resolution, and reduced curl, along with quick drying properties. Surprisingly, such an imageable coating is useful not only for ink-jet imaging but as a universal, or multipurpose imaging film, also useful with devices such as xerographic copiers, color laser copiers, laser printers and the like.

#### Summary Of The Invention

The invention provides a universal imaging material comprising at least one cationic latex emulsion having less than 10 mol% of a copolymerizable monomer having a tertamino or a quaternary ammonium functionality.

The invention further provides a universal imaging sheet comprising a substrate having two major surfaces, wherein at least one of such surfaces has coated thereon an imageable composition having been formed from at least one cationic latex emulsion having less than 10 mol% of a copolymerizable monomer having a tertamino or a quaternary ammonium functionality.

More specifically, universal imaging materials of the invention comprise latex emulsions containing up to 10 mol % of a monomer possessing cationic or quaternary ammonium functionality, and which in addition may contain greater than 10 mol % of a monomer having hydroxy functionality.

The universal imaging sheet is formed in two stages. The first stage is concerned with the synthesis of a specific cationic latex emulsion. The second stage is concerned with the incorporation of the latex of the first stage into a formulation to be subsequently coated onto a suitable substrate.

Synthesis of the latex is achieved by formulating a premix of monomers intended as the components of the final polymer, together with an initiator. A small portion of this

premix is then added to a vessel containing water, a surfactant and more initiator. The reaction vessel is heated until formation of a polymer emulsion starts, and then the remainder of the premix added over an extended time period. Following the addition of all the premix, the whole mixture may be maintained at a predetermined temperature for a suitable time period to ensure complete reaction of all monomers. Preferably all the reactants should be degassed, and the entire reaction carried out in a nitrogen atmosphere.

To use the latex emulsion generated above, the latex may be added to a solution of other suitable polymers, mixing carefully, followed by the addition of other materials such as additional mordants, surfactants, particulates, and if desired, pigments. The final formulation may then be coated by any of a number of well-known techniques onto film base or other substrate, and the coated layer dried. The dried sheets may then be imaged in a wide variety of imaging devices.

As used herein, these terms have the following meanings.

1. The term "synthetic latex" means a latex formed by emulsion polymerization and having a small particle size; a true colloidal suspension.
2. The term "emulsion" means a stable mixture of two or more immiscible liquids held in suspension by small percentages of emulsifiers, and having a continuous phase and a disperse phase.
3. The term "universal imaging material" means a material which is imageable on a variety of types of imaging devices, including but not limited to inkjet, plain paper copier, colored and black/white laser printers and copiers, and is synonymous with "multipurpose". The use of this term with regard to a material does not mean that the material will invariably be imageable on each and every imaging device, or type thereof commercially available or imaginable, but rather than it will provide quality images on more than one type of device.
4. The term "cationic" means having a net positive charge.
5. The term "mudcrack" is used in the industry, and refers to an image defect that appear under a microscope as a series of cracks in a solid image. This has an appearance similar to that seen when wet mud dries. It is thought to be caused by low cohesion of imaging layers.

6. The term "mol%" means 
$$\frac{wt\ \%}{mol\ wt.}$$

Detailed Description Of The Invention

Latex emulsions are useful for a number of convenient reasons. The conditions of reaction need not be overly severe, indeed many of the preparations may be carried out at or near room temperature, and pressurized reaction vessels may not be needed. Water is the most widely-used reaction medium, providing a heat transfer means, that with reasonable reaction rates, may only necessitate the provision of a condenser system attached to the reaction vessel to ensure adequate cooling. The final product, being a suspension in a liquid, is easily transported, has a high concentration of polymer present and, due to the form of the polymer being in small particles dispersed in an aqueous medium, has a relatively low viscosity. Latex materials have proved valuable in such environmentally sensitive products as paints, where the high concentration of polymer, in an innocuous carrier vehicle, has resulted in a superior and widely-used product.

The form of the polymer particles in a latex emulsion is generally spherical with mean particle sizes of below 500 nanometers. Suspensions containing particle sizes in this range, i.e. below the wavelength of light are nearly or completely transparent. Indeed, one monitoring means used during the early part of the polymerization reaction is to look for the appearance of a slight blue coloration to the reaction bulk. This indicates that particulate is forming at approximately the correct particle size.

A colloidal suspension of a monomer is generated in an aqueous medium by agitating a liquid monomer and a surfactant with water. The surfactant enables the monomer to be dispersed as very fine globules of liquid, and the presence of an initiator causes polymerization of each globule independent of other globules. The result is to generate a dispersion in water of very small polymer particles. Size of the solid particles may be much less than that of the liquid monomer globules, and it may be hypothesized that on polymerization of the monomer, the formed polymer is rendered insoluble in the monomer, and is ejected from the original globule into the aqueous environment where it is stabilized by the surfactant. Size may be quite variable, but typical particle diameters are 50-400 nanometers, preferably from 50 to 150, more preferably from 75 to 125 nm.

Particles are preferred for this invention that are considerably below the wavelength of light, as these particles scatter only a minimum of light resulting in clear coatings.

A wide variety of monomers may be used as starting materials for latex emulsion manufacture. Vinyl monomers such as vinyl acetate, vinyl butyrate, vinyl chloride, and the like may be employed as components of latex emulsions, as may urethane monomers, acrylate monomers and many others.

5           Of particular interest to the practice of this invention are acrylate monomers such as ethyl acrylate, methyl acrylate, butyl acrylate, methyl methacrylate, hydroxypropyl acrylate, hydroxyethyl acrylate, and quaternary salts of dimethylaminoethyl acrylate.

          A key feature of this invention is the presence in the latex emulsion of quaternary nitrogen entities. These are present as a positively charged quadruple-bonded nitrogen  
10   atom, and associated therewith a negatively-charged counter ion. These may be selected from a wide variety of anionic entities, for example chloride and other halide ions, sulfate ions, phosphate ions, organic acid ion, such as acetic and propionic, ions combining both traditionally organic entities and traditionally inorganic entities in combination such as methyl sulfate ions and the like. The most convenient, but not the only way, of  
15   incorporating the desired amounts of quaternary nitrogen functions into the latex is, by incorporation in the initial and unpolymerized monomer mix, a monomer suitably substituted with a quaternary nitrogen. An alternative method would of course be to incorporate a suitable monomer that could be further reacted to attach quaternary functions.

20           It is also customary to include hydrophilic polymers in imageable coatings, especially those designed for use with ink-jet devices. Such polymers include polyvinyl pyrrolidone, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, hydroxyethyl cellulose, sodium carboxymethyl cellulose, gelatin and the like. These polymers swell on contact with the aqueous ink providing a semi-rigid layer that is at  
25   least partially immune to physical damage. At a later stage, dependent on storage conditions, the water content of the ink will evaporate, and the polymer will return to its previous unswollen state. However it has been found in practice that while many of these hydrophilic polymer are most efficient in absorbing water, their physical strength progressively deteriorates as they swell, and this condition can be ameliorated by  
30   incorporation of other polymeric materials. Such materials may be hydrophilic themselves, or merely be compatible with the hydrophilic polymers present. Polyvinyl alcohol is one such polymer, having water-affinitive properties itself, but not being so

readily soluble as for example, polyvinyl pyrrolidone. Polymers compatible with the hydrophilic polymers may be present as emulsion latexes, and have been found to induce valuable strengthening properties to the coatings.

Cross linking may also be employed to improve layer strength either covalently or ionically. Such constructions give rise to highly effective coatings, possessing rapid water-absorption characteristics, but also having excellent wet strength.

It is also normal to include other components designed to effect further improvements in performance. One such additional component is a mordant, a material designed to react with the dyes contained in the ink and render them non-diffusing.

Diffusion of the dyes after imaging results in the spreading of colors from one area to another, often seen as apparent broadening of fine lines during storage. Such effects are often amplified by storage in high humidity and temperature conditions. Many mordants are known to dye technology. Inorganic oxides, hydroxides and salts may be used, and their mode of action is predicated on their ability to react with water soluble dyes, to form what are described in the textile industry as "lakes", these generally being considered to be the inorganic salt of a dye. The inks employed in ink jet printing generally contain organic dyes rendered water soluble by the incorporation in the dye structure of an acid function, a preferred acid function being a sulfonic acid group. One or more of these acid groups attached to an organic dye may render it sufficiently soluble in water to render the dye suitable for formulating an aqueous ink. Incorporation of the sulfonic acid group in the dye structure is not the only way in which a dye may be rendered more water soluble. Carboxylic acid groups can perform a similar function, as may quaternary ammonium groups, or hydroxy groups. Sulfonic acid groups have found considerable favor in ink jet inks, and accordingly coatings have been formulated containing components specifically selected to react with the sulfonic acid-containing dyes. Alumina and aluminum hydroxides have been used as mordants, as being relatively innocuous materials, as have salts of long alkyl-chain quaternary ammonium compounds, and polymeric quaternary ammonium compounds. One such mordant, that has found particular favor in the compositions of this invention, is disclosed in U.S. Patent Number 5,342,688. This patent describes a family of mordants based around a polymer having multiple guanidine functionalities.

Imageable coatings may beneficially contain other components, including, for example, plasticizers, surfactants and particulates. Plasticizers found particularly beneficial for the constructions of this invention include polyhydroxy materials exemplified by xylitol, glycerol, mannitol, pentaerythritol gluconic acid and trimethylol propane. Surfactants may be added to aid both the coating process and the ink wetting and distribution properties of the final product. Favored among surfactants and wetting agents are those containing fluorocarbon functions, for example Zonyl FSO 100 (CAS # 65545-80-4) made by DuPont Company, and having a CA index name of poly(oxy-1,2-ethanedial), .alpha.-hydro-.omega.-hydroxy-, ether with .alpha.-fluoro-omega.-(2-hydroxyethyl)poly(difluoromethylene) (1:1).

Particulates found useful in these constructions include polymeric microspheres or beads including poly(methyl methacrylate) beads and other made by the methods of U.S. Pat. No. 5,238,736.

Coating methods for materials of this type include knife coating, wire bar coating, gravure coating, extrusion coating and any process suitable for coating layers of the required thickness.

While the practice of this invention is primarily directed towards receptor coatings for inks, the universal features of this invention make it suitable for use with other imaging processes. Among these imaging processes is to be included electrophotographic methods, as embodied in the copier products of the, among others, Xerox Company, and the Laser Printer products of many companies, for example those of the Hewlett Packard Company and Canon, Inc. These processes function by the photo-initiated removal of electrostatic charge from the surface of a photoconductor, and by using the remaining charge to attract an appropriately-charged toner powder. An image-wise distribution of colored or black toner powder is achieved, which is then transferred by any one of a number of means to a receptor sheet. To permanently adhere the toner powder to the receptor sheet, a fusing step is then initiated. Fusing may be by means of pressure, solvent vapor, heat or the presently preferred method of heating under moderate pressure. It can be argued that the requirements for successful fusing depend on the development of adhesion of the toner to the receptor sheet, rather than by the absorption into the bulk of the layer of a dyestuff carried by a solvent. Mechanisms for toner adhesion to a receptor sheet include, compatibility and intermixing of the toner and

receptor resins to some degree, and the keying of the toner to the receptor surface induced by a degree of roughness of that surface. Naturally for transparent materials, the roughness must be of such scale as to scatter light a minimum amount only. Such a requirement would dictate a roughness whose variations would be less than the wavelength of light. For known toner receptive coatings, such as those embodied by U.S. Patent Nos. 5,310,595 and 5,310,591, coatings tailored specifically for toner adhesion under heat and mild pressure are disclosed, and may use the core-shell components disclosed in U. S. Patent No. 5,500,457. These are coatings designed to promote adhesion and have little or no capacity for absorption of inks. Such materials function poorly as ink jet receptor films.

The practice of the invention may be divided into two stages, which may be separate in both space and time; the formation of the latex and the making and coating of the imageable coating onto a substrate. The latex emulsion made in the first stage is stable for a considerable period of time, so that it may be manufactured at some convenient facility and if needed shipped to a second facility and stored until it is needed for the second stage of practice of the invention. The two stages will be described sequentially in detail.

Details of the general methods of preparation of latex emulsions may be found in Sorenson and Cambell's *Preparative Methods of Polymer Chemistry* (Interscience, 1961) page 158 and page 172, "Emulsion Polymerization of Vinyl Acetate" and in *Encyclopedia of Polymer Science and Engineering* (John Wiley and Sons, 1986) Volume 6, page 1 ff "Emulsion Polymerization".

To form the latex, a glass vessel is charged with distilled or deionized water, a chosen mixture of monomers, a surfactant and an initiator. This mixture is then vigorously stirred to create droplets of globules of monomer. At the end of this stage, further monomer and initiator may be added and the vessel heated to initiate the polymerization step. At the commencement of this step, additional monomer mix may be added over an extended period, and when complete the whole may be maintained at the chosen temperature for several hours to ensure complete reaction. The contents of the reaction vessel are then cooled and the finished latex emulsion decanted for storage or shipment.

It will be apparent that a complex process such as that described above is capable of many modifications, e.g., monomer ratios, temperature, initiator concentrations, agitation, addition rates and times, and the like. Those familiar with the art will be aware that considerable modification of the properties of the final latex emulsion may be brought about by subtle alterations of the process. For example, U.S. Patent No. 5,624,747 discloses what is known as a core/shell latex, so made as to have a particle exterior different in chemical composition and physical properties from the interior of the same particle, such differences being brought about by varying the composition and order of addition of the various materials used.

The transparent film substrate is preferably formed from any polymer capable of forming a self-supporting sheet, e.g., films of cellulose esters such as cellulose triacetate or diacetate, polystyrene, polyamides, vinyl chloride polymers and copolymers, polyolefin and polyallomer polymers and copolymers, polysulphones, polycarbonates, polyesters, and blends thereof. Suitable films may be produced from polyesters obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters in which the alkyl group contains up to about 6 carbon atoms, e.g., terephthalic acid, isophthalic, phthalic, 2,5-, 2,6-, and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, with one or more glycols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and the like.

Preferred film substrates or backings are cellulose triacetate or cellulose diacetate, poly(ethylene naphthalate), polyesters, especially poly(ethylene terephthalate), and polystyrene films. Poly(ethylene terephthalate) is most preferred. It is preferred that film substrates have a caliper ranging from 50  $\mu\text{m}$  to 200  $\mu\text{m}$ . Film substrates having a caliper of less than 50  $\mu\text{m}$  are difficult to handle using conventional methods for graphic materials. Film substrates having calipers over 200  $\mu\text{m}$  are stiffer, and present feeding difficulties in certain commercially available ink jet printers and pen plotters.

When polyester film substrates are used, they can be biaxially oriented to impart molecular orientation, and may also be heat set for dimensional stability during fusion of the image to the support. These films may be produced by any conventional extrusion method.

The substrate may be opaque or transparent; a normally transparent film forming polymeric material may be rendered opaque by the addition of a pigment such as talc,

clay, titanium dioxide, diatomaceous earth, silica, zinc oxide, calcium carbonate, and the like.

Less preferred are paper substrates; however, they may be used if desired.

To promote adhesion of the ink-receptive layer to the substrate, it may be desirable to treat the surface of the film backing with one or more primers, in single or multiple layers. Useful primers include those known to have a swelling effect on a film substrate polymer. Examples include halogenated phenols dissolved in organic solvents. Alternatively, the surface of the film backing may be modified by treatment such as corona treatment or plasma treatment.

The primer layer, when used, should be relatively thin, preferably less than 2 micrometers, most preferably less than 1 micrometer, and may be coated by conventional coating methods.

Transparencies of the invention are particularly useful in the production of imaged transparencies for viewing in a transmission mode, e.g., in association with an overhead projector.

The following examples are illustrative of the invention, and should not be considered limiting. The skilled artisan will easily be able to think of variations. The scope of the invention is that recited in the claims.

#### Test Methods

##### Curl

Curl at 15°C and 20% Relative Humidity is measured by placing a sheet of film in a controlled environment chamber at the conditions mentioned previously, and allowing it to remain there for 24 hours. The film sample is then taken to a controlled environment chamber at 24°C and 50% Relative Humidity, and placed on a horizontal surface. After 30 seconds, the height in millimeters above the surface is measured for each corner, and an average calculated. This measurement is repeated at 1, 2, 3, and 4 minutes, and the largest average recorded is reported as the Curl.

Curl under the conditions of 24°C and 50% Relative Humidity, and 35°C and 80% Relative Humidity is measured in controlled environment chambers set to those conditions. A 3M model 9550 overhead projector is allowed to run for 30 minutes, by which time the stage will have attained an equilibrium temperature. A sheet of unimaged film, imageable side up, is placed on the projector stage, and after one minute the height

of each corner, in millimeters, above the stage is measured and recorded. The average of these 4 values is reported as Curl, the environmental conditions under which it was measured being reported also.

#### Toner Adhesion, Crease Method

5 Toner adhesion was measured by a test that consists of folding a solid black image area 180 degrees down the center, with the toner image on the outside of the fold, rolling the fold 3 times with a one kilogram rubber roller, and rubbing the crease line with a paper towel. Toner is removed from the crease line, and the width of the removed toner area is a measure of the adhesion of the toner to the coating. When compared to a  
10 product specifically formulated for use in a Plain Paper copier similar toner adhesion values were obtained.

#### Examples

##### Example 1

This example discloses the synthesis of a multi-monomer cationic latex polymer.  
15 Three monomers were used for this synthesis: ethyl acrylate, ("EA"), (CAS # 140-88-5), Hydroxypropyl acrylate ("HPA"), (CAS # 25584-83-2) and dimethylaminoethyl acrylate methyl chloride quaternary (referred to as "FA"). All quantities will be given as parts by weight unless otherwise stated.

A reaction vessel was fitted with a condenser, a thermometer, a dropping funnel,  
20 a mechanical stirrer and a nitrogen purging system. To this vessel was added 393 parts of deionized water, 5 parts of cetyl trimethyl ammonium chloride (as a 25% solution in water) and 0.4 parts of V-50. V-50 is an initiator supplied by Wako Chemicals USA Inc., and is 2,2'-azobis(2-amidinopropane) dihydrochloride, CAS # 2997-92-4. The solution was left to stir at 300 rpm. In a separate container a pre-mix of 66 parts of ethyl  
25 acrylate, 30 parts of hydroxypropyl acrylate, 5 parts of dimethylaminoethyl acrylate methyl chloride quaternary (as 80% solids in water) and 0.4 parts of V-50 was made. 10 parts of this pre-mix were added to the reaction vessel, and the vessel contents heated to 50°C. A bluish coloration appeared indicating the formation of a latex emulsion. The remainder of the pre-mix was added over a period of 2 hours. The reaction mixture was  
30 then maintained at the same temperature for a further 4 hours. The reaction was carried out under a steady purge of nitrogen gas. Completion of the reaction was monitored by

percent solids measurement. The contents of the reactor were cooled and decanted into a storage container.

### Example 2

A series of latex emulsion polymers was made by the method of Example 1. The  
5 respective compositions are shown in Table 1 below.

Table 1

Monomer ratios of latex emulsion polymers (by weight)

Emulsion #	Monomers	Ratios
2a	ethyl acrylate/hydroxypropyl acrylate/FA	66/30/4
2b	butyl acrylate/ethyl acrylate/hydroxypropyl acrylate	43/27/30
2c	Ethyl acrylate/hydroxypropyl acrylate/FA	50/30/20
2d	Ethyl acrylate/hydroxypropyl acrylate/FA	60/30/10
2e	ethyl acrylate/hydroxypropyl acrylate/DMAEMA-C16*	60/30/10
2f	ethyl acrylate/hydroxypropyl acrylate/ DMAEMA-C16*	50/30/20

→ \* DMAEMA-C16 is Dimethylaminoethyl methacrylate hexadecyl chloride quaternary.

It should be noted that 2b contains no quaternizable monomers, but may contain  
10 some cetyl trimethyl ammonium chloride.

Table 2 gives monomer ratios by mol%.

Table 2

Monomer ratios in latex emulsions by mol %

Emulsion #	Monomers	Ratios
2a	EA/HPA/FA	72.4/25.3/2.3
2b	BA/EA/HPA	40.1/32.3/27.6
→ 2c	EA/HPA/FA	60.0/27.6/12.4
2d	EA/HPA/FA	68.0/26.15/5.85
2e	EA/HPA/DMAEMA-C16	70.2/27.0/2.8
→ 2f	EA/HPA/DMAEMA-C16	64.22/29.64/6.14

15 The Emulsion #2a was selected for examination in a coating.

Example 3

To aid formulation of experimental coatings, the various components were first made up into pre-mixes, and quantities of the pre-mixes combined to make the final coating solution.

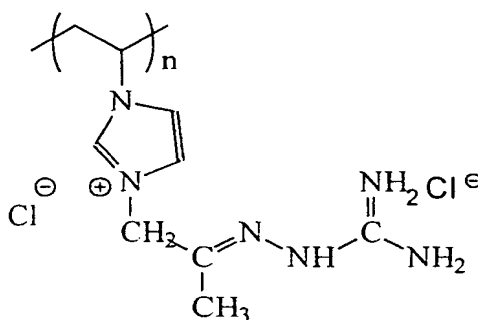
5 The following pre-mixes were made up:

20% aluminum oxide aqueous dispersion, Dispal® 23N4, CondeaVista Chemical Co.;

8% by weight aqueous solution of hydroxypropyl methyl cellulose, available as

Methocel® K-35 made by Dow Chemical Company;

14% by weight aqueous solution of a mordant in water, having the following formula;



10

25% solution of aqueous Xylitol.

A basic coating formulation was then made as shown in Table 3.

Table 3

Ink jet coating formulation

Component	Actual weight g.
Dispal 23N4 dispersion	595.0
Methocel K-35 solution	2167.5
Mordant	121.4
Xylitol solution	136.0
PMMA beads slurry	34.0
De-ionized water	941.1

15

A coating was made of the above formulation, with no addition of a latex emulsion, to produce a coating weight of about 9 g/m<sup>2</sup>. The coating was made on primed polyester film base, having a caliper of 100 microns. This coating served as a control.

Subsequent coatings were made in a similar manner, but with increasing amounts of a 20% by weight aqueous latex made according to the 2a preparation of Example 2 above. This emulsion contained 2.3 mol% of quaternary monomer. These coatings were formulated according to Table 4 below:

5

Table 4Quaternary latex emulsion concentration series

Coating number	Amount of Table 3 formulation	Amount of 20% latex
501-1 (control)	3400.0 g	0.0 g
501-2	3400.0	170.0
501-3	3400.0	340.0
501-4	3400.0	510.0

All coatings had an approximate dry coating weight of 9 g/m<sup>2</sup>.

They were evaluated in a number standard tests, representative data being given in Table 5 below: Mudcracking is an image defect that appear under a microscope as a series of cracks in a solid image. It is evaluated visually; a zero value indicates that the defect is not present.

10

Table 5Performance of coatings of Table 4 in a Hewlett Packard HP 690C printer

Coating No.	Clear Haze	Mud Crack	Curl 70/50	Curl 95/80	Curl 60/20
501-1 (control)	3.4%	0.0	15 mm	20 mm	20 mm
502-2	3.6	0.0	10	16	18
503-3	3.6	0.0	7	12	11
504-4	3.6	0.0	7	9	6

continued.....

Coating number	Black density	Black dry time	Cyan dry time
501-1 (control)	1.92	2.7 min	8.0 min
501-2	1.81	2.8	4.4
501-3	1.72	2.6	4.1
501-4	1.59	2.8	7.7

15

Table 6 gives data for the same series of coatings imaged in a Hewlett Packard HP 870C printer.

Table 6  
Performance of coatings of Table 4 in a Hewlett Packard 870C printer

Coating number	Mud crack	Black density	Cyan density	Cyan dry time
501-1 (control)	0.5	2.15	2.32	7.0 min
501-2	0.5	1.97	2.33	7.0
501-3	1.5	1.64	2.30	7.0
501-4	2.0	1.37	1.97	7.0

5

Clear Haze and Curl data are not included in Table 6 as they are a function of the unimaged film and are independent of printer.

This data serves to both show that all coatings were functioning adequately as ink jet receptor sheets and that coatings containing emulsion latex have improved Curl.

- 10 Specifically, Curl was measured under three conditions: 21°C and 50% relative humidity (RH), 35°C and 80% RH, and 18°C and 20% RH. A low number (measured in millimeters) represents a low degree of Curl, low Curl being desirable. The first set of conditions are those likely to be found in an average office environment, the second set of conditions are representative of tropical environments, and are the most severe
- 15 conditions likely to be found where ink jet printers are in use, and the third set of conditions may be found in latitudes where winters are cold, resulting in very low humidities. The tropical condition is the one where a coating of this type may be expected to have absorbed much water from the atmosphere, and the winter climate condition where the coating may be expected to have absorbed the least. Under all
- 20 conditions, an increased quantity of the cationic latex emulsion leads to decreased curl.

#### Example 4

- A similar coating to the above was made using a commercially-available cationic resin, i.e., Witcobond W-213, available from the Witco Corporation as a 40% latex emulsion in water. It is described as an "aliphatic urethane with surface cationic
- 25 functions". The exact chemical nature of this material is not revealed. It was diluted

with de-ionized water to 20% by weight solids for use. Table 7 gives details of the formulation. Percentage parts by weight in the dry layer are given.

Table 7

Dispal® 23N4 (alumina dispersion)	35.00 % parts by weigh
Methocel® K-35 (cellulose derivative)	39.20
Witco W-213 (cationic urethane latex)	9.80
Xylitol	10.00
Mordant P-134	5.00
PMMA beads	<u>1.00</u>
Total	100.00

- 5            This formulation was coated at 10% by weight solids at a nominal wet coating thickness of 150 microns, yielding a dry coating weight of 15 g/square meter.

This coating was imaged in HP Deskjet 500 printer and gave bright color images, with acceptable dry times. There was only a small degree of curl present.

Example 5

- 10           A coating was made according to the formulation given in Table 8.

Table 8

Component	Percentage parts by weight in dry layer
Methocel K-35	49.1
Cationic Latex (2a in Example 2)	32.7
Xylitol	10.0
Mordant	5.0
Zonyl FSO	2.0
PMMA beads	1.2

- 15           This formulation was coated out of water onto 100 micron glossy opaque polyester film using an extrusion coating method to a dry coating weight of 9 g/m<sup>2</sup>. The resulting coating was dried in an air-impingement oven, and converted to 8 1/2 x 11 inch sheets. These sheets were imaged in a Hewlett Packard 870 ink jet printer and in a

Canon BJC620 ink jet printer. Very high quality color images could be produced. These images could be described as "near photographic color quality".

#### Example 6

This example shows alternative chemistry for the cationic latex emulsion, namely the use of a cross-linker. A specific cross-linking agent that may cross-link the latex particles internally (i.e. within the bulk of the particles) or externally (i.e. between the individual particles) or both, is 3-(trimethoxysilyl) propyl methacrylate, CAS 2530-85-0 supplied by the Aldrich Chemical Company (referred to as A-174). It was incorporated in a latex emulsion having the composition ethyl acrylate/hydroxypropyl acrylate/FA (see Example 1)/A-174 in the ratios, by weight, of 66/25/4/5. The latex was made according to the method given in Example 1. It was incorporated in a formulation as in Table 9.

Table 9

Component	Percentage parts by weight in dry coating
Dispal 18N4	40.0
Emulsion, as above	8.8
PVP K-90	35.2
Trimethylol propane (CAS 77-99-6)	10.0
Mordant P-134	4.0
PMMA beads	2.0

This formulation was coated out of water onto 100 micron Polyester film base using an extrusion coating method to a dry coating thickness of 9 microns. The coatings were imaged in HP 690, HP870, Canon BJC-620 and Epson 800 ink jet printers. All printers yielded high-quality color images, suitable for projection on an overhead projector.

#### Example 7

This example shows alternative chemistry for the cationic latex emulsion, namely the use of a polymer made with acrylic acid (AA) as a monomer according to the method of Example 1. The final composition of this polymer was Ethyl acrylate/Hydroxypropyl

acrylate/FA/AA in the ratios by weight 61/30/4/5. It was incorporated in a formulation as shown in Table 10.

Table 10

Component	Percentage parts by weight in dry coating
Methocel ®K-3 5	59.2
PVP K-90	19.7
Emulsion, as above	19.7
Zonyl® FSO	0.3
PMMA beads	1.0

- 5           It was coated, and tested in the same manner as the formulation in Example 6 above, and yielded similar results.

Example 8

- 10           This example shows alternative chemistry for the cationic latex emulsion, except that a heat-activated cross-linker is incorporated in the latex emulsion. The particular crosslinker used in this example is N-methylol acrylamide (NMA), used in the proportions by weight 64/30/4/2, corresponding to ethyl acrylate/hydroxypropyl acrylate/FA/NMA. It was incorporated in a formulation as shown in Table 11.

Table 11

Component	Percentage parts by weight in dry coating
Dispal ®23N4	35.0
Emulsion, as above	9.8
Methocel® K-35	39.2
Xylitol	10.0
Mordant P-134	5.0
PMMA beads	1.0

- 15           This formulation was coated onto 100 micron Polyester film using a knife coater, at a wet coating thickness of 100 microns. The final dry coating thickness was approximately 10 microns. The coating was imaged in a Hewlett-Packard 870 and Canon 620 ink jet printers and yielded bright colorful images of good transparency.

Example 9

This Example demonstrates the use of alternative water-soluble resins in combination with the latexes of this invention. 9a illustrates the use of a hydroxypropyl methyl cellulose, 9b the use of polyvinyl pyrrolidone (PVP) and 9c the use of these two polymers in combination. Formulation composition is given in Table 12.

Table 12

Component	Percentage parts by weight in dry coating		
	9a	9b	9c
Dispall 23N4	30	35.0	0.0
Methocel K-35	35.3	0.0	44.4
PVP K-90	0.0	47.2	19.7
Emulsion (2a in Example 2)	15.2	11.8	34.6
Xylitol	10.0	0.0	0.0
Mordant	8.0	4.0	0.0
Zonyl FSO	0.0	0.0	0.3
PMMA beads	1.5	2.0	1.0

These formulations were coated by an extrusion coating method onto 100 micron transparent film base, and dried in an impingement oven. The final dry coating thickness of all coatings was approximately 9 microns. The coating were evaluated by imaging in the following inkjet printers: HP 870, HP 690, Canon 610, and Epson 800. All coatings gave bright, clear images when displayed on an overhead projector.

Example 10

A composition found to give particularly acceptable results in ink jet printers is described by Table 13. It was evaluated in an electrophotographic printer, illustrating the versatility of this composition.

Table 13

Component	Percentage parts by weight in dry coating
Dispal® 23N4	35.0
Methocel® K-35	39.2
Emulsion (2a from Example 2)	9.8
Mordant P-134	5.0
Xylitol	10.0
PMMA beads	1.0

This formulation was coated by an extrusion bar method onto either white opaque 100 micron film, or onto 100 micron transparent film. Coatings were dried in an impingement oven and evaluated by imaging in a Hewlett Packard Color Laserjet® 5M printer. This is an electrophotographic printer, whereas printers used in previous examples were based on the ink jet printing process.

The coating on white opaque film gave reflection color densities, measured by a Macbeth TR 924 densitometer as shown in Table 14, and the coating on transparent film gave density values, measured with the same instrument, also shown in Table 14.

Table 14

Image color	Opaque film base Density	Transparent film base Density
Cyan	1.1 (to red light)	1.19 (to red light)
Magenta	1.3 (to green light)	1.04 (to green light)
Yellow	0.97 (to blue light)	1.58 (to blue light)
Orange	0.94 (to blue light)	1.36 (to blue light)
Green	0.78 (to red light)	1.15 (to red light)
Blue	0.69 (to red light)	0.93 (to red light)
Black	1.39 (to white light)	1.74 (to white light)

Example 11

This example illustrates the use of the transparent film described in Example 10 in a black and white office copier. A sheet of the transparent material of Example 10 was imaged in a Xerox 1090 Office Copier. Viewed on an overhead projector, the image was of good contrast.

Toner adhesion was measured by a test that consists of folding a solid black image area 180 degrees down the center, with the toner image on the outside of the fold, rolling the fold 3 times with a one kilogram rubber roller, and rubbing the crease line with a paper towel. Toner is removed from the crease line, and the width of the removed  
5 toner area is a measure of the adhesion of the toner to the coating. When compared to a product specifically formulated for use in a Plain Paper copier similar toner adhesion values were obtained. Width in all samples was less than 1 mm, indicating good adhesion.

#### Example 12

10 This example illustrates the use of the transparent film described in Example 10 as a write-on film.

A sheet of the transparent material generated in Example 10 was used as the material for a hand-written overhead visual. It was found to be receptive to both pencil and the pens used for transparency marking. In the case of the marking pen, drying was  
15 sufficiently fast that a few seconds after application of the ink, the image could not be smeared by finger pressure.

#### Example 13

This example illustrates the use of latex emulsions which do not contain hydroxypropyl acrylate, but which instead contain A-174 (3-(trimethoxysilyl) propyl  
20 methacrylate). Table 15 details the percentage parts by weight of the monomer used to synthesize the emulsion latex. Otherwise the synthetic method was as outlined in Example 1.

Table 15

Latex emulsion number	Ethyl acrylate	Hydroxypropyl acrylate	FA	A-174
13a (control)	64	30	4	2
13b	91	0	4	5
13c	86	0	4	10
13d	76	0	4	20
13e	66	0	4	30

Each of the above latex emulsions, 13a to 13e, were formulated in a coating similar to that of Example 10, except that latex emulsion 2a was replaced successively by latex emulsions 13a to 13e. The coating weight of the dried coatings averaged about 9 g/m<sup>2</sup>.

- 5 Coatings were imaged in a Hewlett Packard 870C ink jet printer, and in a Canon BJC620 ink jet printer, and the color densities measured with a Macbeth TR 924 Densitometer. Tables 16 and 17 shown the measured densities from the Hewlett Packard and Canon printers respectively.

Table 16

10 Density of Colors in HP 870C Printer

Coating # (measuring light)	Black (white)	Cyan (red)	Magenta (green)	Yellow (blue)	Green (red)	Red (green)	Blue (red)
13a	2.47	1.90	1.92	1.42	1.53	1.22	1.74
13b	2.65	1.77	1.93	1.42	1.48	1.20	1.77
13c	2.64	1.98	1.91	1.41	1.43	1.21	1.71
13d	2.70	2.14	1.98	1.52	1.40	1.20	1.81
13e	2.59	2.10	2.00	1.49	1.48	1.26	1.88
HP film	2.00	2.00	1.91	1.62	1.49	1.19	1.75

Table 17

Density of Colors in Canon BJC620 Printer

Coating # (measuring fight)	Black (white)	Cyan (red)	Magenta (green)	Yellow (blue)	Green (red)	Red (green)	Blue (red)
13a	1.85	1.83	0.50	0.51	1.60	0.60	1.83
13b	1.81	1.76	0.51	0.49	1.33	0.64	1.77
13c	1.86	1.78	0.58	0.49	1.79	0.70	1.87
13d	1.84	1.86	0.51	0.52	1.69	0.64	1.95
13e	1.82	1.91	0.52	0.49	1.66	0.68	1.92
3M CG3410 film	2.10	1.31	0.63	0.68	1.29	0.78	1.26

What is Claimed is:

1. A multipurpose imageable sheet having a coating on at least one major surface thereof, said coating formed from a composition comprising:
  - a) at least 30 percent by weight of a hydroxyalkyl methyl cellulose having a number molecular weight below 40,000,
  - b) a metal oxide particulate having particles in size less than 500 nm and present in less than 40 percentage parts by weight,
  - c) from 10% to 30% polymeric latex containing up to 10 mol % of a monomer possessing cationic or quaternary ammonium functionality.
2. A multipurpose imageable sheet according to claim 1 further comprising greater than 10 mol % of a monomer having hydroxy functionality selected from the group consisting of xylitol, glycerol, mannitol, pentaerythritol, gluconic acid and trimethylol propane.
3. A multipurpose imageable sheet according to claim 1 wherein said latex comprises particles having an average particle size of from 50 to 150 nanometers.
4. A multipurpose imageable sheet according to claim 1 wherein said polymeric latex is formed from at least one monomer selected from the group consisting of vinyl monomers, urethane monomers, and acrylate monomers.
5. A multipurpose imageable sheet according to claim 1 further comprising a mordant selected from the group consisting of guanidine based mordant and phosphonium based mordants.
6. A multipurpose imageable sheet according to claim 1 further comprising polymeric microspheres.
7. A multipurpose imaging sheet according to claim 1 wherein said composition comprises a self crosslinkable monomer selected from the group consisting of n-methylol acrylamide, alkoxysilane functional acrylate.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/00870

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 624 743 A (MALHOTRA SHADI L) 29 April 1997 see column 7, line 29 - line 37 see column 19, line 15 - line 20 see claims 1,16,20 ---	1-7
A	US 5 693 410 A (MALHOTRA ET AL) 2 December 1997 -see column 9, line 52 see column 13, line 17 - line 35 see column 14, line 17 - column 43 see claim 1 --- -/--	1-7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Inter      nal Application No

PCT/US 99/00870

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 709 976 A (MALHOTRA SHADI L)  20 January 1998  see column 6, line 61 - column 7, line 8  see column 12, line 67 - column 13, line 11  see column 16, line 65 - column 17, line 19  see column 24, line 26  -----</p>	1-7

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/00870

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5624743 A	29-04-1997	NONE	
US 5693410 A	02-12-1997	NONE	
US 5709976 A	20-01-1998	NONE	